

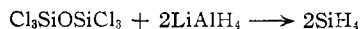
Cleavage of Disiloxanes to Silane by Metal Hydrides

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Disiloxane, $\text{H}_2\text{SiOSiH}_3$, was needed for a molecular spectroscopic investigation.¹ Although this compound can be made readily by hydrolyzing H_2SiCl_2 , the method is unattractive because the starting material is difficult to obtain.² We therefore tried to make disiloxane from hexachlorodisiloxane, $\text{Cl}_6\text{SiOSiCl}_3$, which is readily available from the controlled hydrolysis of silicon tetrachloride.³

An excellent method for converting silicon chlorides to silicon hydrides involves reduction with lithium aluminum hydride in ether.⁴ When we applied this method to hexachlorodisiloxane, reduction and siloxane bond cleavage occurred, with quantitative formation of silane.



Disiloxane itself was similarly cleaved by this reagent. Variation of conditions and use of other metal hydrides also gave no disiloxane from the chloride. The needed disiloxane was therefore prepared by the reported method² in improved yield.

Experimental

Materials and Procedure.—All vacuum manipulations were carried out in a vacuum system similar to that described by Stock,⁵ except that Pyrex stopcocks were used throughout, lubricated with Dow-Corning High Vacuum Silicone grease. Vacuum fractionation of mixtures of products was carried out as described by Sanderson.⁶ Samples were identified by vapor pressure and vapor density measurements, and in questionable cases by comparison of their infrared spectra with spectra of known compounds.

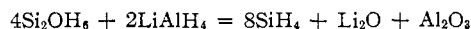
The hexachlorodisiloxane used was prepared by the partial hydrolysis of silicon tetrachloride⁴ at -78° , and separated readily from its higher homologs by fractional distillation at atmospheric pressure. The lithium aluminum hydride was kindly donated by Dr. M. D. Banus of Metal Hydrides Inc., as was the lithium borohydride. Sodium borohydride was purchased from the same company and the sodium hydride was a sample obtained from the du Pont Company. A freshly opened bottle of Mallinckrodt "Analytical Reagent" diethyl ether was found to be dry enough for use as the solvent without further treatment; commercial tetrahydrofuran and dioxane, on the other hand, were purified by fractional distillation and dried by distillation from lithium aluminum hydride.

Disiloxane was prepared by reduction of silicon tetrachloride to silane with lithium aluminum hydride in diethyl

ether, chlorination of the silane with hydrogen chloride and aluminum chloride at 100° , and, after separation of the monochlorosilane from dichlorosilane, hydrolysis of the former. Essentially the same procedure was used in these reactions as Stock has described³ except that yields were improved considerably by decreasing the chlorination time to about 2 hours to suppress the formation of dichlorosilane. Once the monochlorosilane was obtained the yield in the hydrolysis step was increased to 94% by hydrolyzing with the theoretical amount of water at 30° and washing rapidly with about fifty times as much water at 0° .

Reactions with Metal Hydrides.—Lithium aluminum hydride was allowed to react with hexachlorodisiloxane in diethyl ether in two ways. The first method was by sealing the reactants into an evacuated bulb at -195° and then allowing the bulb to warm to room temperature. The reaction was vigorous and took place at about -33° , the melting point of hexachlorodisiloxane. The only volatile product of this reaction was silane, no matter which reagent was used in excess. With excess lithium aluminum hydride the reaction went quantitatively according to the abbreviated equation, given above. The second method of procedure was to slowly add a solution of lithium aluminum hydride in ether or tetrahydrofuran to a solution of hexachlorodisiloxane in the same solvent at 0° and at -40° under 1 atm. of helium. Again silane was the only volatile product. No disiloxane was detected in any case.

In order to determine whether the chlorine atoms were responsible for the vulnerability of the Si-O-Si linkage, disiloxane itself was subjected to treatment in a sealed evacuated tube with lithium aluminum hydride and diethyl ether. Again the molecule was cleaved giving a quantitative yield of silane.



Hexachlorodisiloxane was heated to 120° with lithium aluminum hydride without solvent and refluxed with lithium aluminum hydride in carbon tetrachloride, a non-Lewis base solvent. In the absence of solvent a trace of silane was the only product, and in the carbon tetrachloride there was no reaction until a small amount of dioxane was added; then silane was slowly evolved. This is entirely analogous to the findings of Paddock,⁷ namely, that lithium aluminum hydride would not reduce silicon tetrachloride in the absence of a Lewis base.

With these rather surprising results of the action of lithium aluminum hydride, it was decided that a trial of several other common hydrides might prove interesting and possibly fruitful. Lithium borohydride was used first with the result that hexachlorodisiloxane was again reduced to silane. In this case, however, diborane also was produced—in greater yield than the silane. The ratio of diborane to silane was about 3. No detailed study has been made of this reaction. It was carried out in a sealed evacuated bulb in much the same way as were some of the lithium aluminum hydride reductions.

The last two hydrides examined were sodium borohydride and sodium hydride. Both behaved in about the same manner. Refluxing of the hydrides with hexachlorodisiloxane in dioxane for 4 hours produced no reduction products of hexachlorodisiloxane.

It is clear therefore, that none of the reagents employed in the hope of substituting hydrogen for chlorine in hexachlorodisiloxane were successful in this respect but, instead, in cases where reduction took place, cleavage of the Si-O-Si bonding was effected, giving rise to silane.

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